2.9 The Effect of Lateral Boundary Values on Atmospheric Mercury Simulations with the CMAQ Model

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Abstract Simulation results from three global-scale models of atmospheric mercury have been used to define three sets of initial condition and boundary condition (IC/BC) data for regional-scale model simulations over North America using the Community Multi-scale Air Quality (CMAQ) model. The IC/BC data sets derived from these global models show significant differences in air concentration of mercury species. Variations in the CMAQ model simulation results obtained from each of the three IC/BC data sets provide a measure of the range of certainty regarding patterns of mercury deposition across the study region and the relative importance of domestic versus foreign emission sources responsible for these deposition patterns.

Keywords Atmospheric, global, mercury, modeling, uncertainty

1. Introduction

This paper describes sensitivity testing of a model of atmospheric mercury employed by the U.S. Environmental Protection Agency (EPA) to support environmental regulation. The Community Multi-scale Air Quality (CMAQ) model (Byun and Schere, 2006; Bullock and Brehme, 2002; US EPA, 2005) was used to simulate mercury (Hg) deposition over North America during the entire year of 2001 using three separate initial condition and boundary condition (IC/BC) data sets. These three IC/BC data sets were each developed from simulations of one of three global-scale atmospheric mercury models, the Chemical Transport Model (CTM) adapted for Hg (Shia et al., 1999; Seigneur et al., 2001), the GEOS-Chem model adapted for mercury (Yantosca, 2005; Selin et al., 2007), or the Global-Regional Atmospheric Heavy Metal (GRAHM) model (Dastoor and Larocque, 2004; Ariya et al., 2004). The three patterns of Hg wet deposition simulated by the CMAQ model were all strongly matched to the pattern of the annual precipitation data used in all three cases. However, significant differences did occur in some areas near the boundary, and to a lesser extent at certain locations within the interior of the model domain. This paper investigates the influence of lateral boundary values of

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elemental Hg (Hg^0), reactive gaseous Hg (RGM) and particulate Hg (PHg) concentrations on the simulated total-Hg wet deposition patterns using side-by-side graphical comparisons. The evaluations made here are largely subjective due to the lack of observation of these Hg species, especially aloft. Further study is ongoing to judge whether the boundary values of known oxidants of Hg may also be important.

2. Lateral Boundary Definitions

The CMAQ modeling domain for this study covers most of North America using a Lambert-conformal projection centered at 40° N and 97° W. The lateral boundaries are identified here as "north", "south", "east" and "west" even though these two-dimensional surfaces are not defined in latitude/longitude space. The two-dimensional cross-sections for each lateral boundary are defined using the 14 model layers employed in the CMAQ simulation. These layers are thinner near the surface to better resolve processes in the planetary boundary layer. The boundary cross-sections shown here are scaled in the vertical dimension to the sigma-pressure coordinate system used by the CMAQ model. The horizontal coordinate is based on the row or column position within the horizontal modeling grid and is scaled to match the associated deposition maps. Mercury species concentrations are given either in terms of mol/mol fractions (specifically parts per trillion) or in terms of Hg mass per volume of air at STP conditions (specifically picograms Hg per cubic meter of air at 1 atm and 273.15 K).

3. Description of the Graphical Comparisons

Figure 1 shows a graphical analysis of RGM boundary concentrations and the resulting Hg wet deposition patterns as simulated by the CMAQ model for each of the three IC/BC cases. For each IC/BC case (CTM, GEOS-Chem and GRAHM), the four lateral cross-sections are show with the edge adjacent to the map representing the surface layer values. Figures 2 and 3 show similar comparisons of simulated Hg wet deposition to lateral boundary cross-sections for PHg and Hg^0, respectively. In all of these figures, the vertical coordinate for the lateral boundary cross-sections extends from the surface at the edge next to the wet deposition map to the CMAQ model top at the opposite edge. The patterns of Hg wet deposition simulated for the three IC/BC cases are similar to the annual precipitation pattern expected from climatology and all three CMAQ simulations used the same meteorological input data. However, some significant differences are evident in certain locations.

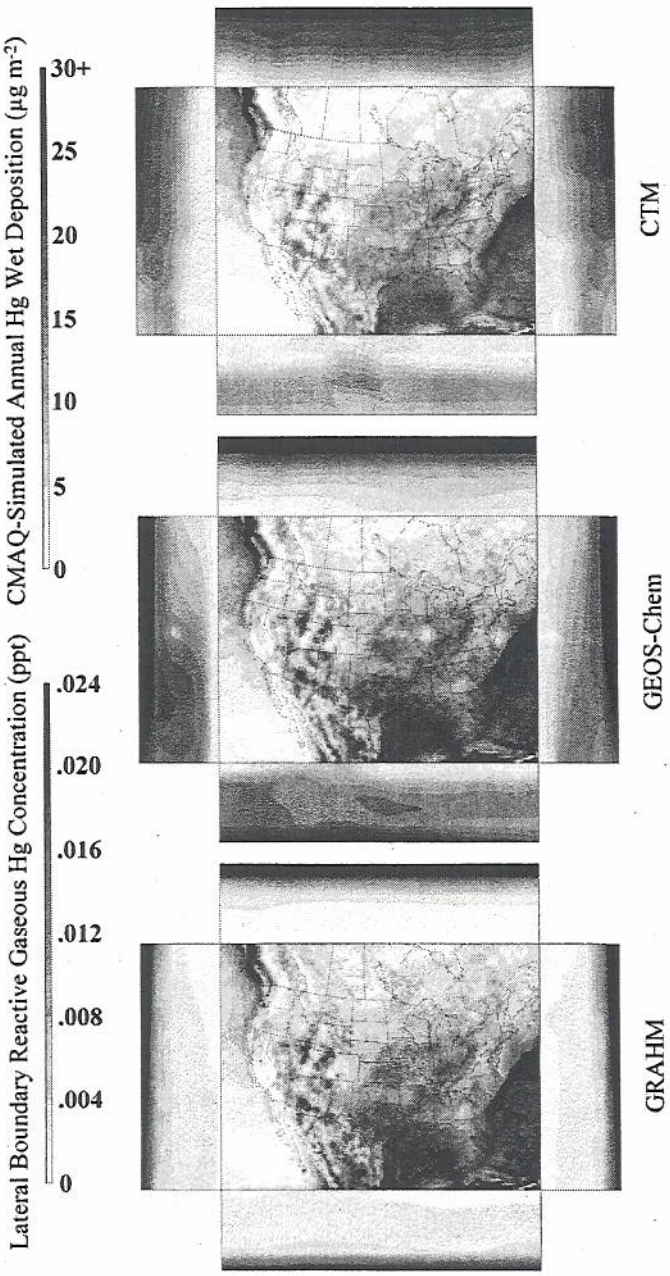

Fig. 1 CMAQ-simulated Hg wet deposition map surrounded by lateral boundary cross-sections for RGM air concentration. Cross-section edges adjacent to the wet deposition map represent the surface-level while the opposite edges represent the CMAQ model top

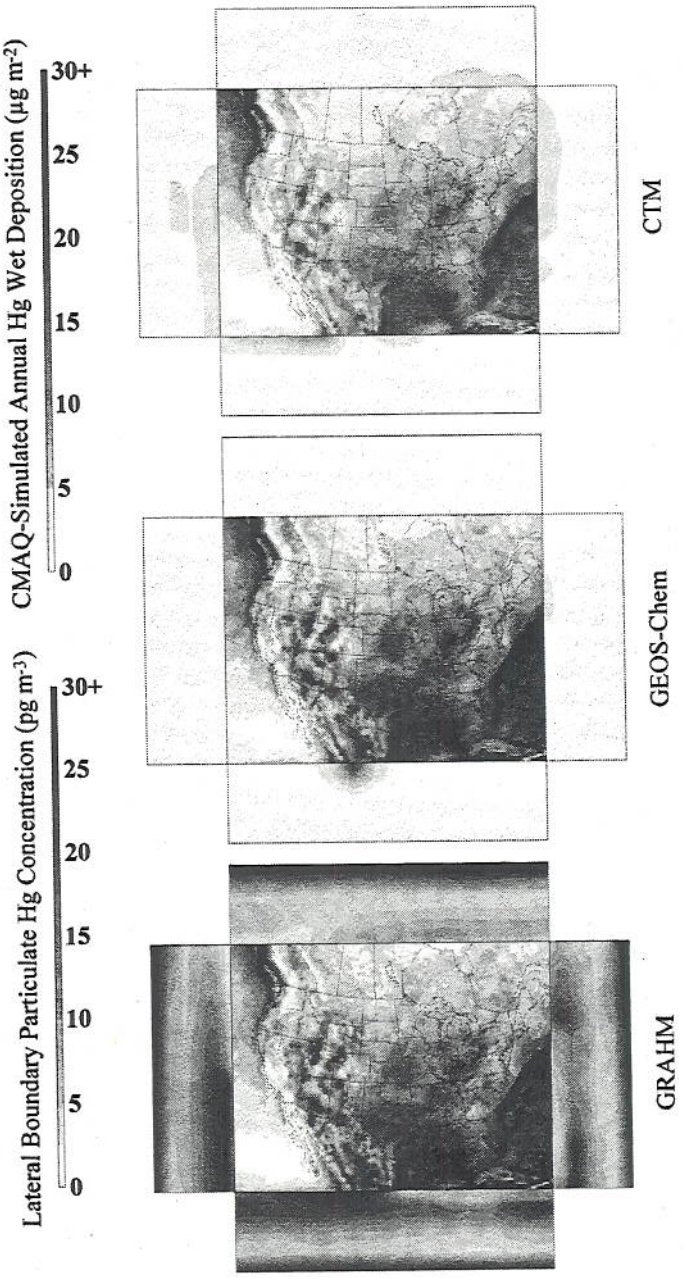

Fig. 2 CMAQ-simulated Hg wet deposition map surrounded by lateral boundary cross-sections for PHg air concentration. Cross-section edges adjacent to the wet deposition map represent the surface-level while the opposite edges represent the CMAQ model top

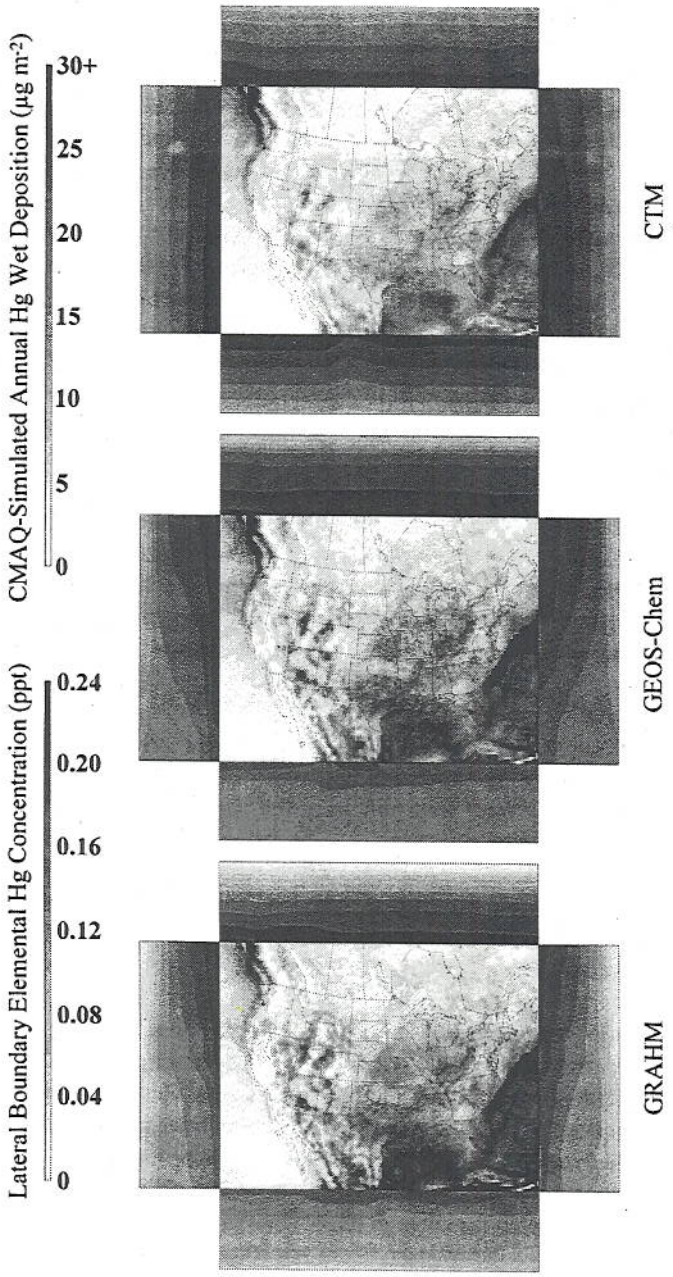

Fig. 3 CMAQ-simulated Hg wet deposition map surrounded by lateral boundary cross-sections for Hg^0 air concentration. Cross-section edges adjacent to the wet deposition map represent the surface-level while the opposite edges represent the CMAQ model top

South-Central and Southeastern Areas: The greatest difference is over the Gulf of Mexico and the Gulf Stream waters where wet deposition flux is significantly lower for the CTM case as compared to GEOS-Chem and GRAHM. Land areas over the south-central and southeast U.S. also show differences, but to a lesser degree. During the warm seasons when precipitation is more abundant and Hg is more efficiently deposited in rain (Hoyer et al., 1995; Keeler and Hoyer, 1997), these areas often have wind flow from the southeast. One might expect RGM and/or PHg flowing from the southeast to be responsible for much of the Hg wet deposition simulated in the Gulf of Mexico and Gulf Stream waters. Figure 1 does show the GEOS-Chem IC/BC set to have generally higher RGM concentrations through the depth of the modeled atmosphere than the other two sets at these boundaries, and the GRAHM IC/BC set shows very high RGM concentrations at high altitudes where warm-season convection can be an effective scavenger. Figure 2 shows the CTM and GEOS-Chem sets have almost no PHg along any boundary, while the GRAHM set has significant PHg concentrations, especially at high altitude. The evidence in Figures 1 and 2 suggests that the CMAQ simulation of Hg wet deposition in the south-central and southeastern areas is sensitive to RGM concentrations at adjacent boundaries and may also be sensitive to PHg there too. Figure 3 shows the highest adjacent boundary values for Hg^0 in the CTM case which also shows the least Hg wet deposition. Influx of Hg^0 from the south and east boundaries does not seem to contribute much to Hg wet deposition in this part of the model domain.

Midwest and Ohio Valley: These areas are well inside the CMAQ model domain, but they also show slightly higher Hg wet deposition for the GEOS-Chem and GRAHM IC/BC cases. Due to the prevailing west-to-east wind flow in central North America, one might expect transport from the western boundary to be most important. However, these areas are usually quite dry when air masses arrive from across the Rocky Mountains. They receive most of their precipitation from moist air transported northward from the Gulf of Mexico. Therefore, it is reasonable to conclude that they would be subject to much the same boundary value effects as the south-central and southeastern regions discussed above.

Inter-mountain West: Areas of heavier Hg wet deposition near Salt Lake City and Phoenix are most intense in the GEOS-Chem and GRAHM cases, much like what was found for the Gulf of Mexico and Gulf Stream waters. However, precipitation here is usually associated with wind flows from the southwest quadrant. Figure 1 shows the GEOS-Chem set to have slightly more RGM along the western boundary than the other sets overall, but the GRAHM set has very high RGM concentrations at high altitude. The CTM set also shows high RGM concentrations at high altitude, but mostly in the northern part of the western boundary. Figure 2 shows high PHg concentrations only in the GRAHM set. Considering the strong solar radiation and possible in-situ production of mercury oxidants like ozone and hydroxyl radical in this area, Hg^0 boundary concentrations could be more important here than in most other areas. Figure 3 shows no great differences in Hg^0 boundary concentrations between the IC/BC sets. Therefore it is difficult to draw any conclusions here about which Hg species is most important in terms of boundary value concentrations.

Coastal British Columbia: This area is nestled in the northwestern corner of the CMAQ modeling domain and, as such, should be more subject to boundary effects than the other areas discussed above. However, the differences between the IC/BC cases in their simulated Hg wet deposition in this area is not as great as one might expect. Unlike the previous areas discussed, here the CTM case appears to have about the same amount of Hg deposition as the GEOS-Chem case, and the GRAHM case shows the least Hg wet deposition of all cases. Since Figure 2 shows the GRAHM case is the only one with significant PHg concentrations at any boundary, this would indicate that in-flux of PHg is not a significant factor to the simulated wet deposition of Hg in this area. Figure 3 shows the boundary concentrations of Hg^0 near this area are lowest in the CTM set, but the CTM simulation case shows nearly the same high intensity of Hg wet deposition as the GEOS-Chem case. Once again, Figure 1 seems to indicate RGM boundary concentrations to be a significant factor in Hg wet deposition. All three boundary concentration sets show high RGM concentrations at high altitude, but the GRAHM set has significantly lower RGM concentrations in the middle and lower atmosphere. It appears that the precipitation processes active in this area may not be scavenging high altitude RGM with the same effectiveness as in the warmer and more convective areas of the eastern U.S. and southeastern coastal regions. Thus, the lack of RGM in the middle and lower layers leads to considerably less Hg wet deposition.

4. Conclusions

The results presented here suggest that the RGM concentrations specified at the lateral boundaries of limited-area atmospheric modeling domains have a significant effect on the intensity of Hg wet deposition simulated by the CMAQ model, not only near the boundary but also in interior regions of the domain. Boundary and lateral concentrations specified for the other mercury species modeled in this study, namely PHg and Hg^0, may also impact subsequent simulations of wet deposition. It is difficult to draw firm conclusions without also considering the effect of boundary concentrations of known oxidants of mercury, and this issue is being investigated as a follow-on to the work described here. It is interesting that the variability in Hg wet deposition between the IC/BC cases investigated here (~30%) is of the same general magnitude as the inter-annual variability that has been seen in Mercury Deposition Network observations (see http://nadp.sws.uiuc.edu/mdn/maps/). One conclusion that can be drawn from the evidence provided here is that realistic lateral boundary air concentrations for Hg and its reactants are necessary in order to expect realistic simulations of Hg wet deposition.

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References

Ariya P, Dastoor A, Amyot M, Schroeder W, Barrie L, Anlauf K, Raofie F, Ryzhkov A, Davignon D, Lalonde J, Steffen A. (2004) Arctic: A sink for mercury. *Tellus*, 56B: 397–403.

Bullock OR, Brehme KA (2002) Atmospheric mercury simulation using the CMAQ model: formulation, description, and analysis of wet deposition results. Atmospheric Environment, 36: 2135–2146.

Byun D, Schere KL (2006) Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multi-scale Air Quality (CMAQ) modeling system. Applied Mechanics Reviews, 59: 51–77.

Dastoor AP, Larocque Y (2004) Global circulation of atmospheric mercury: a modeling study. Atmospheric Environment, 38, 147–161.

Hoyer M, Burke J, Keeler G (1995) Atmospheric sources, transport and deposition of mercury in Michigan: two years of event precipitation. Water, Air, and Soil Pollution, 80: 199–208.

Keeler GJ, Hoyer M (1997) Recent measurements of atmospheric mercury in the Great Lakes region. In: Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters. (Baker JE, editor), SETAC Press, Pensacola, FL, 477 pp.

Landis MS, Keeler GJ (1997) A critical evaluation of an automatic wet-only precipitation collector for mercury and trace element determinations. Environmental Science and Technology, 31: 2610–2615.

Seigneur C, Karamchandani P, Lohman K, Vijayaraghavan K, Shia R-L (2001) Multiscale modeling of the atmospheric fate and transport of mercury. Journal of Geophysical Research 106(D21): 27795–27809.

Selin NE, Jacob DJ, Park RJ, Yantosca RM, Strode S, Jaegle L, Jaffe D (2007) Chemical cycling and deposition of atmospheric mercury: global constraints from observations. Journal of Geophysical Research, 112: D02308, doi:10.1029/2006JD007450.

Shia RL, Seigneur C, Pai P, Ko M, Sze ND (1999) Global simulation of atmospheric mercury concentrations and deposition fluxes. Journal of Geophysical Research, 104(D19): 23747–23760.

US EPA (2005) Technical Support Document for the Final Clean Air Mercury Rule: Air Quality Modeling. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. U.S. EPA web document http://www.epa.gov/ttn/atw/utility/aqm_oar-2002-0056-6130.pdf

Yantosca B (2005) GEOS-Chem v7-03-06 User's Guide, Atmospheric Chemistry Modeling Group, Harvard University, Cambridge, MA, posted 8 November 2005 at http://www-as.harvard.edu/chemistry/trop/geos/doc/man/index.html

Discussion

A. Venkatram:

Are you distinguishing between mixing ratio and concentration in terms of mass per unit volume? Mixing ratio of Hg^{2+} could be high but absolute concentration could be low compared to surface levels.

O. Bullock:

Yes, I am considering concentrations of all gases in terms of molecular mixing ratio to take into account the decreasing density of air with increasing altitude. For particulate Hg, the models all report concentrations in terms of Hg mass per volume of air at standard temperature and pressure. Measurements of all Hg species are usually reported in units of Hg mass per volume, but the amount of air sampled is often metered using mass-flow controllers and these measurements are really in units of Hg mass per volume of "standard" air. However, this scaling to "standard" air has not always been properly noted.

G. Kallos:

RGM concentrations cannot be explained by LRT through the boundaries. The uncertainties can be partially (at least) attributed to differences in surface like SST. Do they use climatological SST fields? Is the same source of SST for all their models?

O. Bullock:

The global models applied in this study were applied independently and I do not know if they used the same source of information for sea surface temperature. I agree that high RGM concentrations cannot be explained by long range transport alone, but LRT could be a contributing factor for the RGM concentrations in some cases.

J. Pleim:

The wet deposition seems to be driven by deep convective precipitation. How about the ground level concentrations? Are these CMAQ results similarly different among the three simulations driven by the three different global models?

O. Bullock:

Whenever precipitation of any kind is present, the CMAQ model simulates very little RGM and particulate Hg, but elemental mercury can still exist in significant concentrations due to its low solubility in water. Because RGM dry deposits so rapidly, its simulated concentration near the ground is usually low except near emission sources and when vertical mixing within the PBL is strong so that RGM from aloft is being brought down to the surface. Ground level concentrations of RGM are not strongly dependent on the global model being used to set the boundary values. Much the same is true for particulate mercury, but elemental mercury concentrations at the ground, and at all levels, is dependent on the global model providing boundary conditions.